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Si-rich-SiO_2 layers with high excess silicon content: light emission and structural properties

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Abstract

Si-rich-SiO_2 layers with high excess Si content grown by radio-frequency magnetron sputtering were studied by Raman scattering, X-Ray diffraction, electron paramagnetic resonance, and photoluminescence methods. It was found that high temperature annealing stimulates the formation of Si crystallites with preferred orientation in <111> direction. It was shown that the effect of crystallites orientation depends on excess Si content. Besides, comparable contribution of amorphous and crystalline silicon phases in the structure was observed for the annealed layers with Si excess more than 55%. It was observed that both crystalline and amorphous Si inclusions give the essential contribution to the photoluminescence spectra.

Keywords: Si-rich-SiO_2, magnetron sputtering, crystallites, photoluminescence, EPR, XRD.

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1. Introduction

The special attention is attracted to Si-rich-SiO_2 layers that could contain both nanocrystalline and amorphous Si inclusions. The interest in such layers is concerned with effective light emission ability in the visible and near infrared region at room temperature [1-5]. Many models were proposed to explain bright emission of these structures in wide spectral range at room temperature. And only few investigations were devoted to the elucidation of the mechanism responsible for the formation of Si crystallites in such systems. At the same time Si inclusions could be effective activators of different defects located in oxide matrix, in particular, silicon oxide defects [2, 6, 7] or the impurities such as rare-earth ions [8]. It was shown that the intensity of oxide-related emission could be comparable with the silicon-related one [1, 2].

In spite of numerous publications devoted to the investigations of Si-rich-SiO_2 structures, the majority of them concerns the case when the content of excess Si, C_{Si}, is less than 30 % [4, 7-9]. However, as it was shown in [10, 11] the processes responsible for the formation of the light emission properties of the layers with higher Si excess can differ. Moreover it was found that the highest PL efficiency is observed for the layers with C_{Si}=40-45% [11]. Therefore, the investigation of the layers with C_{Si} higher than 30 % is important for the clarification of the mechanism of light emission process for such layers and for the controllable monitoring of PL parameters for their optoelectronic application. In this work, structural, compositional and light emission properties of the layers with different excess silicon content were investigated and the main attention is devoted to the investigation of the layers with Si excess more than 40 %.

2. Experimental details

Si-rich-SiO_2 layers were grown by radio-frequency magnetron sputtering method in mixed argon-air atmosphere. The sputtering was carried out during 3 hours from two 2-inch space-apart pure Si and SiO_2 targets on a long (150 mm) amorphous quarts (α-SiO_2) or silicon single crystal substrates as described in [6]. The thickness of the layers was in the range of 800-1000 nm, but thicker layers (~4.5 μm) were also investigated. The layers were annealed at 1100 °C during 40 min in nitrogen flow.

Electron paramagnetic resonance (EPR) spectra were measured with Varian-12 spectrometer. X-ray diffraction (XRD) measurements were carried out using D8 Advance

Bruker X-ray diffractometer with an Euler cradle and non-polarized Cu $K_{\alpha1,2}$ radiation. For the measurements standard ϑ-2ϑ symmetric geometry as well as asymmetric grazing geometry for incident beam were used. Raman scattering spectra were measured under excitation by 487.9-nm-line of argon laser as it was described in [2]. PL spectra were excited by 337-nm-line of nitrogen laser and detected by IKS-12 spectrometer coupled with Ge-detector. The PL measurements were performed in the temperature range of 77-300K. All other measurements were carried out at room temperature.

3. Results

3.1. Structural properties

Raman scattering spectra of as-deposited layers demonstrate the presence of amorphous silicon phase only that is confirmed by the observation of the band peaking at 480 cm^{-1}. Its intensity decreases with C_{Si} decrease in the layers. High-temperature annealing leads to the decrease of the intensity of 480-cm^{-1} band that is connected with the amorphous silicon phase. Simultaneously the appearance of the band peaked at 505-517 cm^{-1} in different samples occurs (Fig.1). This band is apparently connected with Si crystallites since its peak position shifts to the low-frequency side with Si excess decrease. The estimation of the sizes of Si crystallites formed during the annealing was done based on the model described [12] and took into account the peak position of the corresponding signal and its full-width at half maximum. The sizes of Si crystallites were found to be in the range of 3-6 nm and they increase with C_{Si} increase. At the same time, it is worth to note that for the layers with C_{Si}>55 % the contribution of 480-cm^{-1} band, caused by amorphous silicon, remains essential even after the high temperature annealing.

XRD patterns obtained in ϑ–2ϑ symmetric geometry for as-deposited and annealed layers demonstrate a narrow diffraction peak for 111 reflection from silicon single crystal substrate (for the layers grown on Si single crystal substrate) or wide diffraction peak in the region of $2\vartheta \cong 22^o$ from quarts substrate (for the layers grown on quarts substrate) (Fig. 2a), respectively. The diffraction signals from Si-rich-SiO_2 layer in symmetric geometry were not well-defined detected owing to low diffraction intensity.

An asymmetric grazing geometry for incident beam was used both to increase the diffracted volume of the layers and to decrease the effect of the substrates, namely, to exclude the diffraction peak from silicon single crystal substrate that will superpose the diffraction peak from Si crystallites (if they are present in the layer deposited on Si substrate) as well as to decrease the influence of amorphous quarts substrate when amorphous silicon phase will detected in the layer deposited on quarts substrate. The angle of incident X-ray beam was varied in the range of 1-7 degrees. In an asymmetric XRD pattern of the annealed layers the broad diffraction peak from amorphous silicon at $2\vartheta \cong 16^o$ and wide peaks at $2\vartheta \cong 28.5^o$ and $2\vartheta \cong 95^o$ that correspond to 111 and 333 reflections for crystalline Si are present (Fig. 2, insert). The peaks at $2\vartheta \cong 28.5^o$ and $2\vartheta \cong 95^o$ are associated with the Si crystallites formation. The absence of any others diffraction peaks for Si crystallites denotes their preferred orientation in <111> direction. In spite of the increase of diffracted volume at the decrease of the angle of incident X-ray beam, the highest intensity of the peaks associated with the Si crystallites was observed for the incidence angle of 4^o for both types of substrate (Fig. 2b, 2c). This fact denotes that disorientation of (111) planes of Si crystallites with respect to substrate surface does not exceed 10^o. The evaluation of the formed Si crystallite size was performed by the use of full width at half maximum (FWHM) for the wide peaks for 111 reflection at $2\vartheta \cong 28.5^o$ from nanocrystalline Si and Debye-Scherrer formula [13]. The sizes of Si crystallites were found in the range of 2.5-5 nm, that in the same range with the sizes estimated from Raman scattering spectra.

EPR spectra measured for the as-deposited layers are dominated by the signal with g=2.0055 (Fig.3, curve 1) that corresponds to the silicon dangling bonds. Its intensity reflects the total number of these centers and linearly increases with C_{Si} (Fig.3, insert).

After annealing two signals appear in EPR spectra. Their intensities increase with C_{Si} (Fig.3, curve 2). One of them is a narrow isotropic line with g=2.0025. The other one is an anisotropic signal with g-factor 2.0057–2.0063 which depends on Si excess. For the layers with C_{Si}>50%, the dependence of EPR spectra on the orientation of magnetic field was found.

3.2. Light emission properties

Usually, no PL emission from as-deposited layers was observed, while after the high-temperature annealing a bright emission in near infrared-visible spectral range was detected. PL spectra of the layers with C_{Si}=35-50% demonstrate one broad band (Fig. 4a, curve 1), which intensity increases with C_{Si} decrease (Fig.4b, curve 1). Simultaneously the peak position shifts to the high-energy side (Fig.4b, curve 2).

PL spectra of the layers with C_{Si}>50% show a broadening and slight shift of PL peak position to the low-energy side with C_{Si} increase, that could be connected with the presence of two radiative channels. Simultaneously the decrease of PL intensity takes place (Fig. 4a, curve 2). Sometimes, two separated PL bands could be observed that proves the last assumption. In this case the peak position of lower-energetic PL band does not depend on the energy of excitation light, while the higher-energetic one demonstrates usually slight shift to the high-energy side with the increase of the excitation energy [14].

This is confirmed also by the measurement of PL spectra at ultraviolet excitation when the information about PL properties could be obtained from subsurface layer. As one can see from Fig.4c, the PL spectrum recorded from the face side of the layer (Fig. 4c, curve 1) demonstrated low energetic peak position in comparison with the spectra obtained from the back-side of the layer (curve2).

The investigation of temperature behavior of PL spectra of the layers with different C_{Si} revealed that the shift of the peak positions of both bands with temperature is similar to the shrinkage of the band gap of bulk silicon (not shown).

4. Discussion

After the high-temperature annealing of the layers with C_{Si}>50% the contribution of amorphous silicon phase to Raman scattering spectra remains essential (Fig.1). This means that in this case not all the excess silicon takes part in the formation of Si crystallites.

The presence of crystalline and amorphous Si phases in such layers after the annealing is also confirmed by EPR spectra. The signal with g-factor of 2.0025 testifies to the formation of the EX-centers that are the feature of the existence of the interface between crystalline Si and SiO_2 host [15]. In the case of the layers grown on Si substrate it could be assigned to the formation of this interface between layer and substrate. However, the observation of EX-centers for the layers grown on quarts substrate means that this interface appeared due to formation of Si crystallites.

The signal with g=2.0057-2.0063 could be attributed to the centers like Si dangling bonds, but its anisotropy gives the possibility to assume that these centers are P_b-like centers, that are known to be feature of Si-SiO_x interface. The dependence of EPR spectra on the direction of the magnetic field observed for the layers with C_{Si}>50% means that the crystallites in such samples have an orientation. As it was shown by XRD measurements the crystallites a preferred orientation is in <111> direction.

It should be noted that the value of g-factor of this signal with g=2.0057-2.0063 decreases with the depth of the layer and approaches to g=2.0055. This accompanied with the vanishing of its anisotropy as it was shown in [2]. The latter could mean that EPR centers located in the depth and responsible for this signal, are Si dangling bonds that are the fingerprint of amorphous Si phase.

Taking into account mentioned above, we could reconstructed the structure of the layers with C_{Si}>55 %. So, we can consider that Si crystallites, somewhat elongated in <111> direction and orientated in the same direction, are covered by silicon oxide and embedded in amorphous silicon matrix. Since the orientation of Si crystallites was found for all the layers deposited on both types of substrates we can assume that the effect of the substrate is negligible. Moreover the orientation of crystallites obviously depends on the distance between them and it disappears when the C_{Si} becomes less than 55%. A similar effect of the orientation of Si crystallites with elongated shape was observed in [16] for the films of amorphous silicon prepared by magnetron sputtering and crystallized under high-temperature annealing. Such shape of Si crystallites was also observed in the Si-rich-SiO_2 layers [17] that were prepared by similar technique as the layers investigated in the present paper. It is possible that in our layers the orientation of Si crystallites is also connected with their non-spherical shape and small distance between them.

The analysis of the structural properties allows supposing that both Si crystallites and amorphous Si phase could give the contribution to PL spectra. In fact, for the layers with high C_{Si} values (more than 50%) two PL bands are observed in PL spectra (Fig.3, curve 2). The intensity of low-energetic PL band decreases with C_{si} decrease, while its peak position does not change practically. At the same time the peak position of high-energetic PL band shifts to high energy side with C_{Si} decrease that is due to the decrease of Si crystallite sizes. It is essential that temperature behavior of both PL bands is similar to the variation of bulk Si band gap that gives the evidence that both PL bands are connected with silicon itself. It can be concluded that the high-energetic PL band is due to Si crystallites, while the low-energetic one can be attributed to amorphous Si. Usually the intensity of the last band is lower than the intensity of crystallite-related PL band. However as it was shown earlier in [10] the intensity of PL band caused by the amorphous silicon can exceed the intensity of crystallite related band after the passivation of Si dangling bonds by hydrogen.

5. Conclusions

Si-SiO_2 layers with high excess Si content prepared by magnetron co-sputtering of Si and SiO_2 on Si or quartz substrates as-deposited and after the high temperature annealing were studied by Raman scattering, XRD, electron paramagnetic resonance and photoluminescence methods. It was shown that the annealed layers besides the Si nanocrystals contain inclusions of amorphous Si phase. Both crystalline and amorphous inclusions give an essential contribution in the photoluminescence spectra. It was found that for the layers with C_{Si} more than 55% the silicon crystallites are oriented. XRD data shows that they are oriented in <111> direction. It is shown that the effect of orientation does not depend on the type of substrate but depends on the excess Si content.

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Figure captions

Fig.1. Raman scattering spectrum of the layer deposited on quarts substrate. C_{Si} = 60 %.

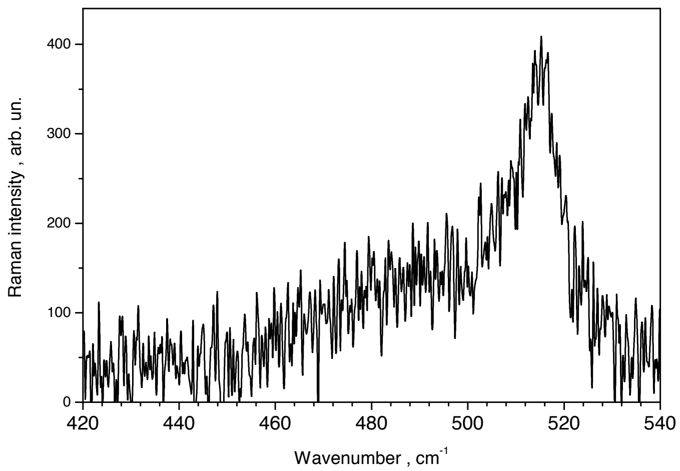
Fig.2. XRD patterns from: (a) amorphous quarts substrate (ϑ–2ϑ geometry); 111 reflection from Si-SiO_2 annealed layers with C_{Si} = 60 % deposited onto silicon (b) and quarts (c) substrates (asymmetric geometry). Insert - asymmetric XRD pattern from Si-SiO_2 annealed layers deposited onto quarts substrate.

Fig.3. EPR spectra for the as-deposited (1) and annealed layer (2) with C_{Si}=60%. Insert – the dependence of the intensity of the signal from Si dangling bonds on C_{Si} for as-deposited layers.

Fig.4. a) PL spectra of the layers with C_{Si}=36% (curve 1) and C_{Si}=55% (curve 2) measured at 300 K under 488-nm excitation wavelength.

b) Variation of total PL intensity (1) and main peak position (2) with C_{Si}. Excitation wavelength is 488 nm.

c) PL spectra of the layers with C_{Si}=60% measured at 337-nm excitation wavelength from face side (curve 1) and back side (curve 2) of the layer.


Raman intensity , arb. un.
Wavenumber , cm^{-1}
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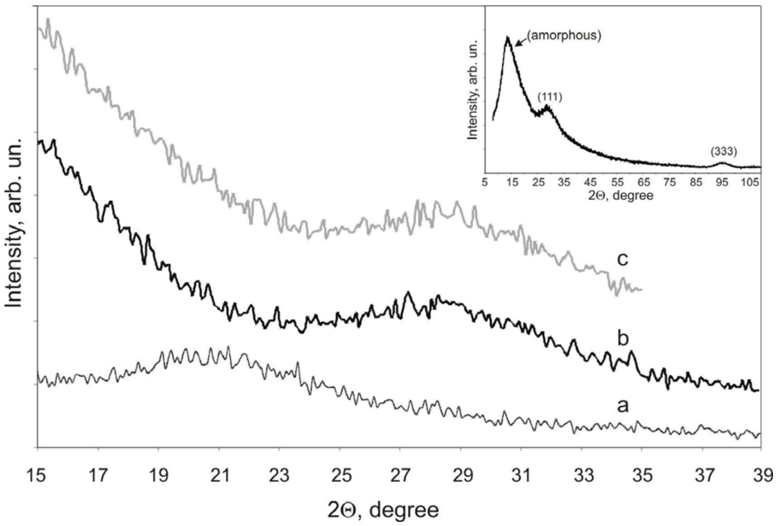
200
300
400
420
440
460
480
500
520
540

Fig. 1


Intensity, arb. un.
2Θ, degree
a
b
c
15
17
19
21
23
25
27
29
31
33
35
37
39
(amorphous)
(111)
(333)
Intensity, arb. un.
2Θ, degree
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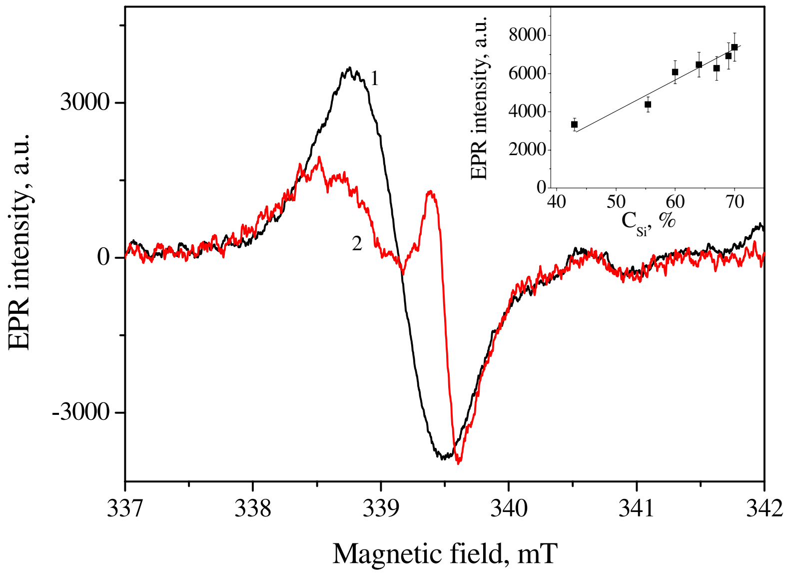
15
25
35
45
55
65
75
85
95
105

Fig. 2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338
339
340
341
342
Magnetic field, mT
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2
EPR intensity, a.u.
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6000
4000
2000
0
40
50
60
70
C$_{Si}$, %

Fig. 3.

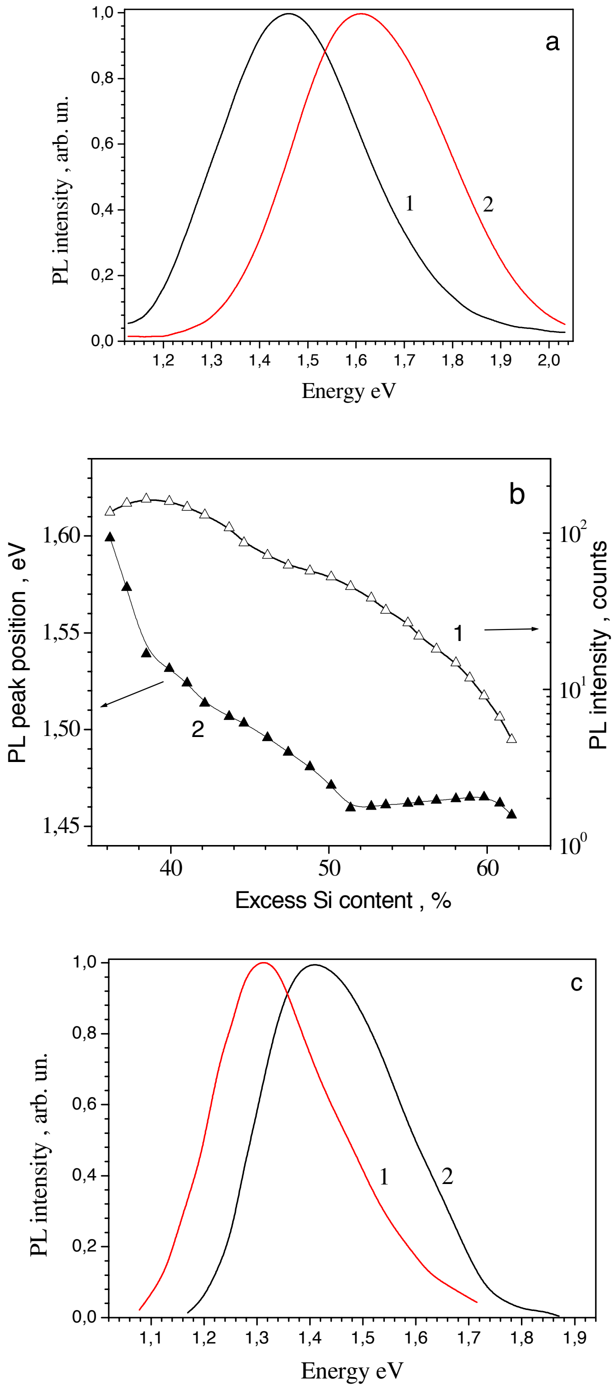
a
PL intensity , arb. un.
Energy eV
1
2
b
PL peak position , eV
PL intensity , counts
Excess Si content , %
1
2
c
PL intensity , arb. un.
Energy eV
1
2

Fig.4